

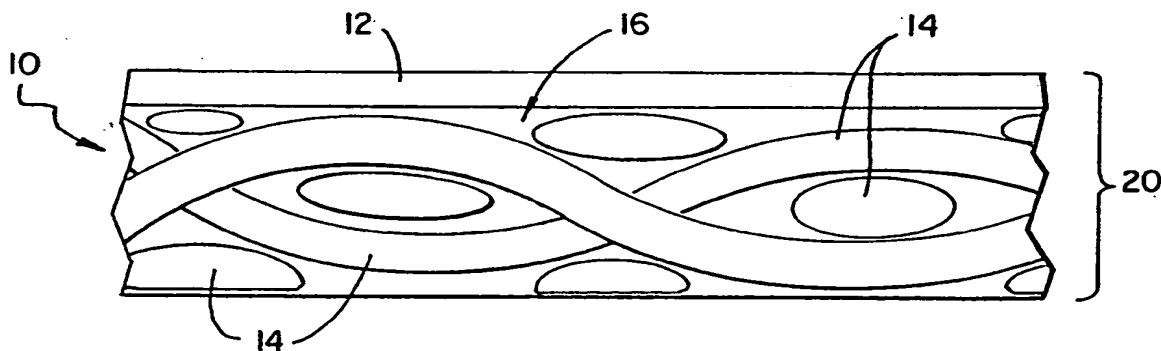


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<p>(21) International Application Number: PCT/US91/08675 (22) International Filing Date: 21 November 1991 (21.11.91) (30) Priority data: 617,195 23 November 1990 (23.11.90) US (71) Applicant: CHEMFAB CORPORATION [US/US]; 701 Daniel Webster Highway, Merrimack, NH 03054 (US). (72) Inventors: EFFENBERGER, John, A. ; 115 Hitching Post Lane, Bedford, NH 03102 (US). KOERBER, Keith, G. ; 39 High Street, Goffstown, NH 03045 (US). ENZIEN, Francis, M. ; 18 Wild Flower Drive, Penacook, NH 03303 (US). CUSHMAN, Michael, P. ; 129 Thornton Road, New Boston, NH 03070 (US). PUNNETT, Milton, B. ; 1075 Luther Road, East Aurora, NY 14052 (US).</p>		<p>(74) Agents: SOLOWAY, Norman, P. et al.; Hayes, Soloway, Hennessey &amp; Hage, 175 Canal Street, Manchester, NH 03101-2335 (US). (81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).  Published With international search report.</p>

*no adhesive*

(54) Title: IMPROVED COMPOSITE MATERIALS FOR ARCHITECTURAL STRUCTURAL END USE



## (57) Abstract

A flexible, reinforced textile composite material for constructing tensioned fabric structures, e.g. for sheltering from the outdoor environment, is disclosed. The material has a hydrophobic protective film element (12) laminated to the textile composite material (10) to provide enhanced hydrophobicity. In a preferred embodiment, of the invention, one or a mixture of colorants, dyestuffs or biological agents are incorporated into the hydrophobic protective film layer. The textile composite material has particular application as a tensioned architectural element for forming a dome, roof or the like, or as an electromagnetic window or a radome.

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1                    IMPROVED COMPOSITE MATERIALS FOR  
2                    ARCHITECTURAL STRUCTURAL END USE

3            The present invention relates to textile products, and  
4 more particularly, to fiber reinforced flexible laminated  
5 fluoropolymer-containing composites suitable for outdoor,  
6 structural use, and to protective structures comprising  
7 flexible fluoropolymer-containing composites. The flexible  
8 fluoropolymer-containing composites of the present invention  
9 have particular utility as structural architectural  
10 materials, e.g. for building "shaded villages" in the  
11 desert, or domes over large sports stadia, churches,  
12 shopping malls, and the like, and in the fabricating of  
13 electromagnetic windows or radomes, and will be described in  
14 connection with such utility, although other utilities are  
15 contemplated.

16           Since their introduction in the early seventies, the use  
17 of flexible fluoropolymer-containing composites as  
18 "architectural materials" for constructing so-called  
19 "tensioned-fabric structures" has continuously grown. This  
20 surge in such application has been associated with the  
21 development of an advanced grade of flexible fluoropolymer-  
22 containing woven fiberglass composite materials having  
23 advantageous mechanical and solar-optical properties along  
24 with good soil-release behavior, virtual incombustibility  
25 and good weatherability. Fluoropolymer-coated flexible  
26 textile substrates, such a polytetrafluoro-  
27 ethylene (PTFE) coated fiberglass or the like, exhibit very  
28 good weathering and uniqueness of physical properties such  
29 as their very low surface free energy and good balance of  
30 solar optical characteristics, favoring their use in  
31 architectural structural applications. These properties,  
32 coupled with the composite material's inherently high  
33 strength to weight ratio, further favors their use in such

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1 structural applications.

2 Particularly important properties of fluoropolymer-  
3 coated flexible textile composites intended for  
4 architectural tensioned-fabric structural end use is their  
5 very low surface free energy and chemical inertness to the  
6 natural elements of rain, wind, snow and solar insulation  
7 and resistance to biological contamination. Specifically,  
8 the extremely low surface free energy of PTFE coated textile  
9 composites confers upon a structure made from such a  
10 fluoropolymer composite the ability to shed adventitious  
11 water and to resist soiling which would otherwise occur as  
12 the result of exposure over time to airborne smog, soot,  
13 aerosols, etc. which are ubiquitous in the outdoor  
14 environment.

15 It has been found that the surface free energy of PTFE  
16 coated fiberglass composites, as manufactured, is about  
17 18-19 ergs/cm<sup>2</sup>, rendering them highly hydrophobic. However,  
18 over time in the outdoors, it has been found that the  
19 surface free energy can increase to about 23 ergs/cm<sup>2</sup> with  
20 occasional areas as high as 28 ergs/cm<sup>2</sup>. While 23 ergs/cm<sup>2</sup>  
21 still represents very good hydrophobicity, it represents a  
22 sub-optimal value given the inherent properties of PTFE, and  
23 may be unacceptably high in structural applications such as  
24 radomes where hydrophobicity is a key to microwave  
25 transmission. As a result, it is necessary to clean the  
26 structure periodically to restore initial appearance and  
27 hydrophobicity.

28 While not wishing to be bound by theory, it is believed  
29 that the increase in surface energy over time is related to  
30 the physical surface topography of the PTFE coated textile  
31 composites. It is known that the coating process itself may  
32 not produce a truly smooth, uniform and defect-free (i.e.  
33 microcracks, craters, pinholes, etc.) polymeric surface. A  
34 direct consequence of the somewhat microcracked surfaces  
35 inherent to these composites when produced by a coating  
36 methodology is the slow deterioration of such release

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1 properties and hydrophobicity. Dirt and microbiological  
2 growth can take a "foothold" in such microcracks,  
3 particularly as such cracks become larger over time and/or  
4 with thermal cycling (diurnal and seasonal). This behavior  
5 is discussed in "The Effects of Rain on a Radome's  
6 Performance", Microwave Journal, May 1986 (John A.  
7 Effenberger, Richard R. Strickland, Edward B. Joy).

8 In order to overcome this problem, it has been proposed  
9 to use a TFE copolymer to heal the microcracking of the PTFE  
10 in the surface of PTFE coated fiberglass composite intended  
11 for architectural use. While useful to a degree, the  
12 improvement obtained with such treatment does not completely  
13 prevent soiling, and to the extent that non-uniformity of  
14 coating, and coating defects occur, a surface with variable  
15 ability to resist soiling or to exhibit optimal  
16 hydrophobicity results, particularly over time in the  
17 outdoor environment.

18 Additionally, since one of the functions of the PTFE in  
19 such coated products is to protect the reinforcing glass  
20 fibers from the elements, particularly from liquid water,  
21 the presence of coating defects such as craters, pinholes,  
22 microcracks, etc. represents a compromise in the effective  
23 strength of the composite itself necessitating the use of  
24 elevated safety factors in designing with such material for  
25 structural use.

26 Another disadvantage associated with PTFE coated  
27 fiberglass composites intended for architectural tensioned-  
28 fabric structural end-use is the limited ability to  
29 incorporate into the composite materials aesthetic effects  
30 such as color. While pigmentation of the PTFE is possible,  
31 such pigmentation is limited by the deleterious effects of  
32 hard, mineral particulates on the effective strength of the  
33 reinforcements when incorporated into the coating  
34 formulations. Thus, the amount and location of pigment  
35 which can be added is severely limited. Additionally,  
36 because of the non-uniform topography of a woven

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1 reinforcement, and the limitations in the dip-coating  
2 process used to produce such composite materials, it is not  
3 possible to produce a dip-coated composite with a uniformly  
4 thin layer of pigment containing PTFE whereby to obtain  
5 uniformly intense coloration by reflected light and yet  
6 retain a high degree of light transmission.

7 Moreover, when color is introduced in a PTFE coating  
8 process, it is difficult to control both the uniformity and  
9 transmissivity of the coated product since the coatings tend  
10 to be thicker in the textile "windows" and thinner over the  
11 textile "knuckles". Thus, while available for industrial  
12 PTFE coated products, colors other than white have not  
13 played a significant role in the aesthetically more  
14 demanding architectural applications of the PTFE coated  
15 products.

16 Generally, the level of pigmentation required to achieve  
17 a uniformly aesthetic effect in a coated product is high  
18 enough to substantially reduce the overall light  
19 transmission of such composites. This is detrimental to its  
20 intended use, for example, as a skylight or solar luminaire.  
21 It is, therefore, an object of the present invention to  
22 provide a flexible textile composite material for tensioned-  
23 fabric structural end-use which overcomes the aforesaid and  
24 other disadvantages of the prior art, and more particularly  
25 to provide flexible fluoropolymer composite materials which  
26 are particularly suited to outdoor, structural end-use, and  
27 which are characterized by durable hydrophobicity, an  
28 ability to resist the deleterious effects of liquid water,  
29 and compatibility with architectural design strategies aimed  
30 at good light transmission and intense coloration by  
31 reflected light.

#### 32 SUMMARY OF THE INVENTION

33 In accordance with the present invention, there is  
34 provided a flexible, laminated, reinforced textile composite  
35 material for structural end-use comprising a fibrous  
36 reinforced load-bearing component, said load-bearing

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1 component comprising a fibrous reinforced fluoropolymer  
2 textile composite material, at least one surface of said  
3 composite material being covered, at least in part, by a  
4 hydrophobic protective film layer laminated thereto. In a  
5 preferred embodiment of the invention, the hydrophobic  
6 protective film comprises PTFE and may include one or more  
7 additives such as a colorant or dyestuff, or a bactericide  
8 such as a fungicide, mildewicide, or the like.

9 Other objects, advantages and features of the present  
10 invention will be apparent and readily understood from the  
11 following description of the invention, taken in conjunction  
12 with the drawings, in which like reference characters refer  
13 to like parts, and wherein:

14 DESCRIPTION OF THE DRAWINGS

15 Fig. 1 is a side elevational view, in cross section, of  
16 a laminated textile composite material made in accordance  
17 with the present invention;

18 Fig. 2 is a side elevational view, in cross section, of  
19 an alternative form of laminated textile composite material  
20 made in accordance with the present invention;

21 Fig. 3 is a side elevational view, partly in section,  
22 showing the use of a laminated textile composite material  
23 made in accordance with a preferred embodiment of the  
24 present invention as a structural element in a domed  
25 structure; and

26 Figs. 4 and 5 illustrate transmittance and reflectance  
27 of a laminated textile composite material made in accordance  
28 with the present invention over a range of electromagnetic  
29 radiation between 190  $\mu\text{m}$  and 900  $\mu\text{m}$ .

30 DETAILED DESCRIPTION OF THE INVENTION

31 As used herein, the term "textile" shall include  
32 naturally occurring and synthetic woven or non-woven  
33 materials such as a knit fabric. Any suitable textile  
34 material capable of withstanding processing temperatures and  
35 able to sustain the static and dynamic mechanical loads in a  
36 structure may be employed as the reinforcing material for

*textile*

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PTFE fibers

1 of load bearing composite in accordance with the present  
2 invention. Examples, include, inter alia, fiberglass,  
3 ceramics, graphite (carbon), PBI (polybenzimidazol),  
4 polyaramides such as KEVLAR and NOMEX, polyolefins such as  
5 TYVEK, polyesters such as REEMAY, polyamides, polyimides,  
6 thermoplastics such as KYNAR (PVF<sub>2</sub>) and TEFZEL (ETFE),  
7 polyethersulfones, polyetherimides, polyetherketones,  
8 novoloid phenolic fibers such as KYNOL, PTFE, cotton, and  
9 other natural and synthetic fibers. The reinforcing  
10 material may comprise a yarn, filament, monofilament, slit  
11 film or the like assembled as a textile. The reinforcing  
12 material also may comprise a metallic material such as steel  
13 wire, mesh or the like. Preferably the reinforcing material  
14 comprises fiberglass.

PTFE film

15 Referring in particular to Fig. 1 of the drawings, there  
16 is illustrated a preferred form of a laminated textile  
17 composite material 20 made in accordance with the present  
18 invention. The textile product comprises a first, load-  
19 bearing composite element 10, having a second layer 12  
20 formed of a polytetrafluoroethylene-containing film layer  
21 laminated to the load bearing element 10.

22 The composite textile substrate layer 10 is formed by  
23 coating or impregnating a textile substrate, e.g. fiberglass  
24 14, with PTFE 16 or the like in known manner, for example,  
25 by applying the PTFE from a suspension and fusing the  
26 applied PTFE for example, in accordance with the teachings  
27 of U.S. Patent 3,928,703 to Cook.

28 The hydrophobic protective film layer 12 preferably  
29 comprises one or more preformed films, at least one of which  
30 comprises a TFE polymer, preferably PTFE, which may be  
31 preformed by a variety of known techniques such as melt  
32 extrusion, melt casting, skiving and paste extrusion.  
33 Additional film elements comprising, for example, the  
34 thermoplastic terpolymer of TFE, HFP and VF<sub>2</sub> may be employed  
35 in combination with the PTFE film.

36 If desired, one or a mixture of additives may be



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1  
2 included in the hydrophobic protective film element 12 for  
3 producing a desired effect. For example, a colorant or dye  
4 stuff may be incorporated into the film material, e.g. prior  
5 to forming the film so that the resultant film comprises a  
6 uniformly dispersed colorant or dye. Also, if desired, one  
7 or a mixture of fungicides, bactericides and mildewicides or  
8 other biocidal agents may be incorporated into the film so  
9 as to result in a film having enhanced resistance to  
10 biological contamination.

11 Referring to Fig. 2, the laminated textile composite  
12 material includes a load-bearing composite textile substrate  
13 element 10, sandwiched between hydrophobic protective film  
14 elements 12A and 12B, each formed of a polytetrafluoro-  
15 ethylene-containing film.

16 Fig. 3 shows the use of the laminated textile composite  
17 material 20 made in accordance with the present invention,  
18 as a structural architectural element, for example, in  
19 forming a dome. As seen in Fig. 3, the laminated composite  
20 material is supported by a supporting frame member 22 with  
21 the film element 12 facing the outdoor environment.

22 The invention, and its advantages may be further seen by  
23 the following non-limiting examples which illustrate a  
24 preferred method of forming a flexible reinforced laminated  
25 composite textile material in accordance with the present  
26 invention. The overall process is as follows:

27 First, the load-bearing textile composite is formed by  
28 impregnating or coating a fabric layer 10 with a  
29 fluoropolymer such as PTFE, TFB (Hoechst), KEL-F (3M), or a  
30 blend thereof, and the impregnating material is fused by  
31 heating the coated/impregnated material.

32 In Example I, film elements 12A and 12B comprise  
33 separately formed cast PTFE films with a thickness of  
34 approximately 4.0 mils.

35 In Example II, a colorant is incorporated into the PTFE  
36 film element.

37 In Example III, the film layers 12A and 12B comprise

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1 separately formed cast 1.7 mil PTFE films in which the  
2 outermost 0.4 mils on one face remain unfused initially.

### 3 EXAMPLE I

#### 4 A. PRODUCTION OF LAMINATE

5 A PTFE coated glass fabric suitable for outdoor,  
6 structural end-use (CHEMFAB's RAYDEL M-26 electromagnetic  
7 window composite) was employed as a substrate element 10  
8 along with a 4 mil perfluoropolymer film element 12 to  
9 create a laminated composite 20 in accordance with the  
10 present invention. Lamination was facilitated by first  
11 applying a top coat of PFA resin to the PTFE coated glass  
12 fabric to provide a melt-bondable surface. The  
13 perfluoropolymer film (DF-1700 PFA available from Chemical  
14 Fabrics Corporation, "CHEMFAB") consisted of 3.8+ mils of  
15 PTFE and 0.1+ mils of PFA on one of its surfaces.

16 Lamination was accomplished by passing a "sandwich"  
17 of the film on both sides of the top-coated substrate such  
18 that the film/substrate interface is PFA-to-PFA between a  
19 succession of heated platens which were set at 400, 600 and  
20 700 degrees F, and finally between cooling platens set at 55  
21 degrees F. At a feed rate of 1.5 ft/min, the exiting  
22 laminate had a temperature of 440-470 degrees F. The  
23 applied pressure in the platens was less than 4 psi, and the  
24 laminating "work" (coated substrate plus films) was  
25 supported between lightly coated TCGF carriers as it passed  
26 between the platens.

27 Properties of the laminated composite (LEOD-87-3) thus  
28 prepared are as follows:

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TABLE I

<u>PROPERTY</u>	<u>UNITS</u>	<u>VALUE (b)</u>
Weight (a)	oz/y <sup>2</sup>	36.0 +/- 0.1
Thickness	.001 in	26.5 +/- 0.3
Tensile Strength	lb/in	
warp		515 +/- 16
fill		496 +/- 29
Tear Strength	(lb)	
warp		40 +/- 2
fill		55 +/- 1

(a) The fiberglass reinforcement of the coated substrate weighed 9 oz/y<sup>2</sup> with warp and fill yarns of ECC 150 2/2 fiberglass at a count of 28 x 29 respectively.

(b) Mean value and standard deviation based on n = 10 (except for weight and thickness for which n = 4).

These are consistent with expectations given that the coated substrate weighed 22.5 oz/y<sup>2</sup> and was 18.0 mils in thickness.

It is well known that the success of PTFE coated fiberglass in outdoor structural end-use is largely due to its inertness to the ubiquitous elements associated with the outdoor environment: namely sunlight (particularly ultra-violet radiation), water (liquid and vapor), and oxidizing gases (oxygen and "smogs"), over a significant range of temperatures.

Experimental data (E. Takabatake; Nitto CHEMFAB Co., Ltd.; Proceedings of the International Association of Shell Structures; Dresden, Germany, September 1990) has confirmed that deterioration of the strength of such PTFE coated fabrics may be accelerated by immersion of such composites in water at elevated temperature. Indeed, liquid water is believed to be a significant causative agent for the slow mechanical deterioration of such composites in outdoor

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1 structural use. Real-time weathering data has indicated  
2 that about 25% of the tensile strength of such coated  
3 composites can be lost after fifteen years. Since such  
4 deterioration necessitates an increase in mechanical design  
5 safety factors governing the outdoor structural use of such  
6 composites, this will in general translate into the need for  
7 heavier, stronger and more costly composites. Thus, there  
8 is a significant premium attached to the use of PTFE coated  
9 composites in such use.

10 B. EVALUATION OF LAMINATE

11 In order to evaluate the laminated PTFE composite of the  
12 present invention for its ability to better resist the  
13 mechanical deterioration induced by liquid water, the  
14 laminate PTFE composite of Example I, Part A, was subjected  
15 to the action of concentrated, aqueous, alkaline solutions.  
16 The elevated pH was employed so that any hydrolysis due to  
17 liquid penetration of the composite would be accelerated.

18 In a preliminary evaluation, a box-like container was  
19 fabricated from the laminate prepared in Example I, Part A,  
20 and filled with 40% aqueous NaOH. The container was then  
21 placed in a hot water bath to maintain the temperature of  
22 its contents at 60-70 degrees C for 8-9 hours on each of  
23 five days with a total exposure extending over seven days.  
24 No effect of such exposure was observed on either the  
25 tensile or tear strength of the laminate.

26 Subsequently, an apparatus was set up to allow a one-  
27 sided exposure of this same laminate to both a 50% aqueous  
28 NaOH solution at 60 +/- 5 degrees C. Also included as a  
29 control in the evaluation was a PTFE coated fiberglass  
30 composite, CHEMFAB's DARLYN® 1100, which is noted for its  
31 outstanding inertness in hot, corrosive, environments.

32 As may be seen from the data of Table II, the laminated  
33 product prepared in accordance with Example I, Part A (based  
34 upon a film comprised of PTFE as well as a coated substrat  
35 comprised of PTFE) is clearly superior in its ability to  
36 remain unaffected by exposure to liquid water even at

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1 elevated pH. This is presumably a reflection of the  
 2 inability of the liquid water to penetrate to the  
 3 reinforcement due to the more perfect state of consolidation  
 4 of the PTFE polymeric matrix when incorporated into the  
 5 composite as a film.

TABLE II

7 (A) Effect Upon Tensile Strength (Warp) of Exposure to  
 8 Aqueous NaOH at 60 +/- 5 degrees C.

TENSILE STRENGTH: (lb/in)			
	Unexposed	Exposure: 259 Hrs.	Exposure: 500 Hrs.
15 LEOD-87-3: 16 (laminated)			
18 Mean	567	519	541
19 Range (1)	564-571	492-544	524-582
21 DARLYN® 1100: 22 (coated)			
24 Mean	1616	1026	709
25 Range (1)	1602-1635	422-1478	391-1123

27 (1) The dramatic increase in the range of measured  
 28 values for the coated PTFE composite (DARLYN® 1100) relative  
 29 to the laminated PTFE (LEOD-87-3) is also indicative of the  
 30 superiority of the laminate to such exposure.

32 (b) Effect Upon Tensile Strength (Warp) of Exposure to  
 33 Aqueous NaOCl at 60 +/- 5 degrees C.

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1			
2		Tensile Strength: (lb/in)	
3		<u>Unexposed</u>	<u>Exposure: 264 Hrs.</u>
4			
5	LEOD-87-3	567	583
6	(laminated)		
7			
8	Darlyn® 1100	1616	1324
9	(coated)		

## EXAMPLE II

### A. PRODUCTION OF LAMINATE

The films employed on each face of this laminate were multilayered PTFE films with one face comprised of PTFE in an unfused condition to promote lamination by the method of copending application Serial No. 305,748, assigned to the common assignee. One film was an all PTFE film; the other film was a multi-layer construction with 0.4 mils of clear PTFE, followed by 0.2 mils of PTFE containing 2% by weight of red iron oxide, and followed again by 0.2 mils of PTFE containing 5% "Velveteen" black carbon. The final 0.2 mils is the clear, unfused PTFE. Thus, the pigment determining the hue of reflected light appear in two layers constituting only 0.4 mils of the overall thickness of the PTFE.

These multilayered films were laminated to a previously formed PTFE coated fabric containing about 70% by weight PTFE and 4.0 oz/y<sup>2</sup> of fiberglass. In accordance with copending application Serial No. 305,748, the outermost 1.24 oz/y<sup>2</sup> of PTFE were left unfused to serve as a bonding layer for the films.

### B. EVALUATION OF LAMINATE

The final laminate weighs 15 oz/y<sup>2</sup> and has a thickness of 10.0 mils with a tensile strength of about 200 x 200 lb/in.

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1 The resulting laminate was tested for light transmission  
2 and reflectivity and the results plotted in Figs. 4 and 5.  
3 An overall transmission of about 7% was observed. This  
4 transmission level is typical of that obtained in a domed  
5 stadium based upon a coated PTFE composite such as  
6 SHEERFILL® II from CHEMFAB.

7 However, the reflectance from one side (the "natural" or  
8 unpigmented side) is 68.5% while that from the side which  
9 has been laminated with a brown pigmented film is 52.1%.

10 This demonstrates the ability to employ pigmented films  
11 to differentially (face to face) control the overall  
12 "shading" (transmission) obtainable from a given composite,  
13 as well as the color and level of reflected light. This is  
14 a highly desirable feature in a skylight material.

15 Also, providing hydrophobic films on both sides of the  
16 textile composite fabric will also render both surfaces of  
17 the installed composite fabric hydrophobic and soil  
18 resistant.

### 19 EXAMPLE III

#### 22 A. PRODUCTION OF LAMINATE

23 The fiberglass reinforcement weight 4 oz/y<sup>2</sup> and is based  
24 on plain woven D450 2/2 yarns at a count of 38 x 36 (warp  
25 and fill). A PTFE coating of 9.8 oz/y<sup>2</sup> was applied by well  
26 known dip coating methodology, except that an additional 1.2  
27 oz/y was applied in a last pass which remained unfused since  
28 the highest processing temperature on that pass was 595  
29 degrees F. A specific gravity of 1.49 +/- .01 was employed  
30 for each dip using Teflon® 3013 and TD 3313 dispersions.

31 The film used in lamination was 1.7 mils thick of which  
32 the outermost 0.4 mils on one face remained unfused. A  
33 layer of film was laminated to each face of the coated  
34 substrate, mediated by the unfused PTFE surfaces of each  
35 component using the lamination techniques described in  
36 Example 1.

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## 1 B. EVALUATION OF LAMINATE

2 The final laminate was tested in a Q-UV(B) accelerated  
 3 weathering tester, the contact angle to water determined by  
 4 means of a Gonometer, and the results reported in Table III.

5 TABLE III

6 Effect of Q-UV Exposure on Laminated PTFE Composites(2)

8 Time of	Contact Angle(2)	Relative
9 Exposure(1)	to Water	Hydrophobicity
10 (hrs)	(degrees)	(RH)(3)
11		
12 0	97.1	1.000
13 214	104.2	1.346
14 602	103.6	1.308
15 824	105.1	1.400
16 1013	109.2	1.707

17  
 18 (1) Total elapsed time of exposure about one half of which  
 19 in exposure to UV-B radiation; the other half involves  
 20 an aqueous spray, absent radiation.

21 (2) Unconnected for grantational effects at angles about 90  
 22 degrees.

23 (3) Calculated from  $\cos^4 \theta_o/2$  where  $\theta$  = contact angle

$$24 \quad RH = \frac{\cos^4 \theta_o/2}{\cos^4 \theta_t/2}$$

25  
 26 Defined in this way higher values of relative  
 27 hydrophobicity correspond to lower values of surface  
 28 free energy.

29 This increase in relative hydrophobicity upon exposure in a  
 30 Q-UV(B) accelerated weathering tester is unlike the decrease  
 31 reported for conventionally coated PTFE composites.

32 The observed durable hydrophobicity makes such a product  
 33 an outstanding structural composite based on its relative  
 34 low surface energy and therefore soil-releasing capability.

35 Various changes may be made in accordance with the  
 36 foregoing invention without departing from the spirit and  
 37 scope of the present invention.



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CLAIMS

1. A structure comprising a supporting element holding a tensioned textile composite material comprising a fibrous reinforced load-bearing element (10), and having at least one surface thereof covered, at least in part, by  
5 at least one hydrophobic protective film element (12) comprising TFE polymers laminated thereto.
2. A structure as claimed in claim 1 wherein said fibrous reinforced load-bearing element (10) is sandwiched between hydrophobic protective film elements (12a, 12b) laminated thereto.
3. A structure according to claim 1 or 2 wherein said hydrophobic protective film element (12) includes a colorant or dyestuff.
4. A structure according to any of claims 1 to 3 wherein said hydrophobic protective film element (12) includes a biological agent, preferably a fungicide, a bactericide or a mildewicide.
5. A structure according to any of claims 1 to 4 wherein said hydrophobic protective film element (12) comprises a fluoropolymer film, preferably a cast PTFE film, a skived PTFE film, or a paste-extruded PTFE film.
6. A structure according to any of claims 1 to 5 in the form of a dome, roof, atria, skylight or architectural accent, preferably an electromagnetic window or radome or an environmental enclosure or shelter.
7. A composite material according to any of claims 1 to 6 wherein said fibrous reinforced load-bearing element (10) comprises a textile material selected from natural and synthetic fibers, preferably fiberglass.
8. A reinforced textile composite material according to any of claims 1 to 6 wherein said fibrous reinforced load-bearing element (10) is selected from a metal, a graphite and a ceramic.

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9. A reinforced textile composite material according to any of claims 1 to 8 wherein said fibrous reinforced load-bearing element (10) is in the form of a fiber, a filament, a slit film or a yarn, assembled as a textile.

10. In an architectural material for constructing tensioned fabric structures, said material comprising a flexible, laminated, reinforced textile composite comprising a fibrous reinforced load-bearing element (10),  
5 the improvement wherein at least one surface of said load-bearing element is covered, at least in part, by at least one hydrophobic protective film element (12) comprised of a TFE polymer.

11. In an architectural material according to claim 10, the improvement wherein said load-bearing element (10) is sandwiched between hydrophobic protective film elements (12a, 12b) laminated thereto.

12. In an architectural material according to claim 10 or 11, the improvement wherein said hydrophobic protective film element (12) comprises one or a mixture of colorants or dyestuffs.

13. In an architectural material according to any of claims 10 to 12, the improvement wherein said additive material comprises a biological agent, preferably a fungicide, a bactericide or a mildewicide.

14. In an architectural material according to any of claims 10 to 13, the improvement wherein said fibrous reinforced load-bearing element (10) comprises a textile material selected from the group consisting of natural and  
5 synthetic fibers, preferably fiberglass.

15. In an architectural textile composite material according to any of claims 10 to 13, the improvement wherein said hydrophobic protective film element (12) comprises a fluoropolymer film, preferably a cast PTFE  
5 film, a skived PTFE film, or a paste-extruded PTFE film.

16. In an architectural textile composite material according to any of claims 10 to 14, the improvement wherein said fibrous reinforced load-bearing element (10)

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is selected from the group consisting of a metal, a  
5 graphite or a ceramic.

17. In an architectural textile composite material  
according to any of claims 10 to 16, the improvement  
wherein said fibrous reinforced load-bearing element (10)  
is in the form of a fiber, a filament, a slit film or a  
5 yarn, assembled as a textile.

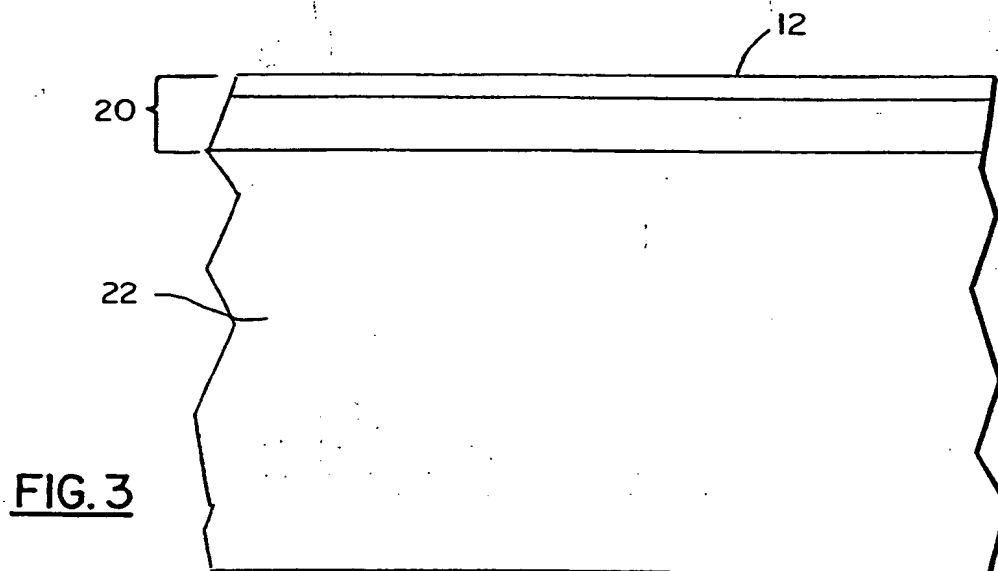
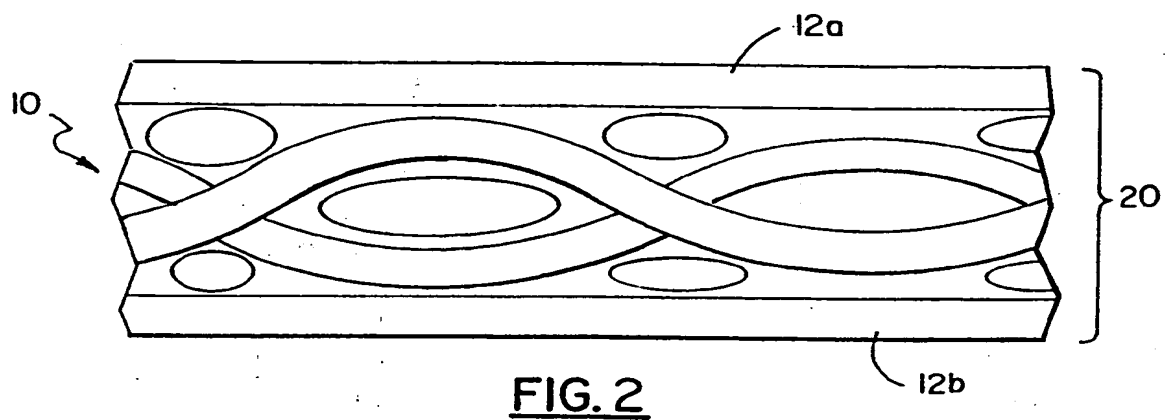
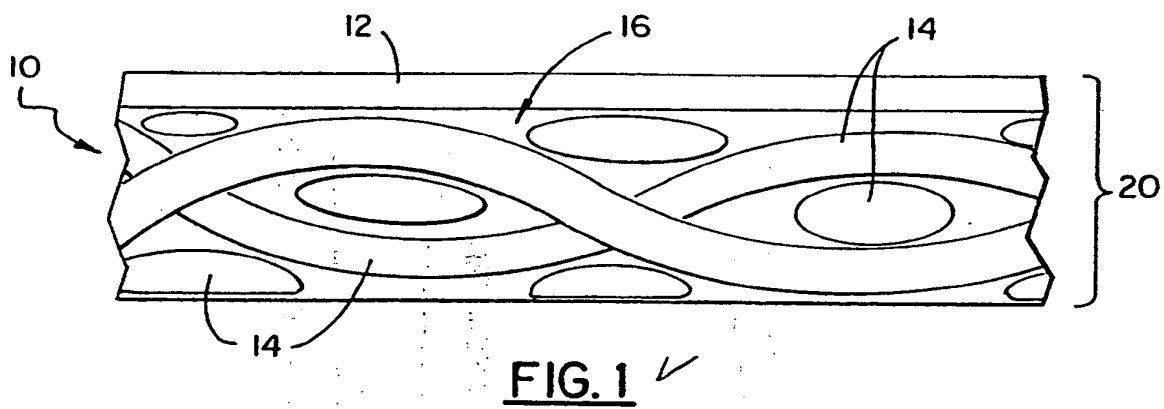
18. In an architectural textile composite material  
according to any of claims 10 to 17, the improvement  
wherein said hydrophobic protective film element (12)  
comprises a plurality of film elements (20) laminated to  
5 one another.

19. In an architectural textile composite material  
according to claim 18, the improvement wherein at least  
the film element (12) outer-most of said laminate (20)  
comprises PTFE.

20. In an architectural textile composite material  
according to claim 19, the improvement wherein one or more  
film elements interior of said outer-most element (12)  
comprises one or a mixture of colorants, dyestuffs and  
5 biological agents.

21. A structure according to any of claims 1 to 9,  
wherein said film element (12) comprises a plurality of  
film elements (20) laminated to one another.

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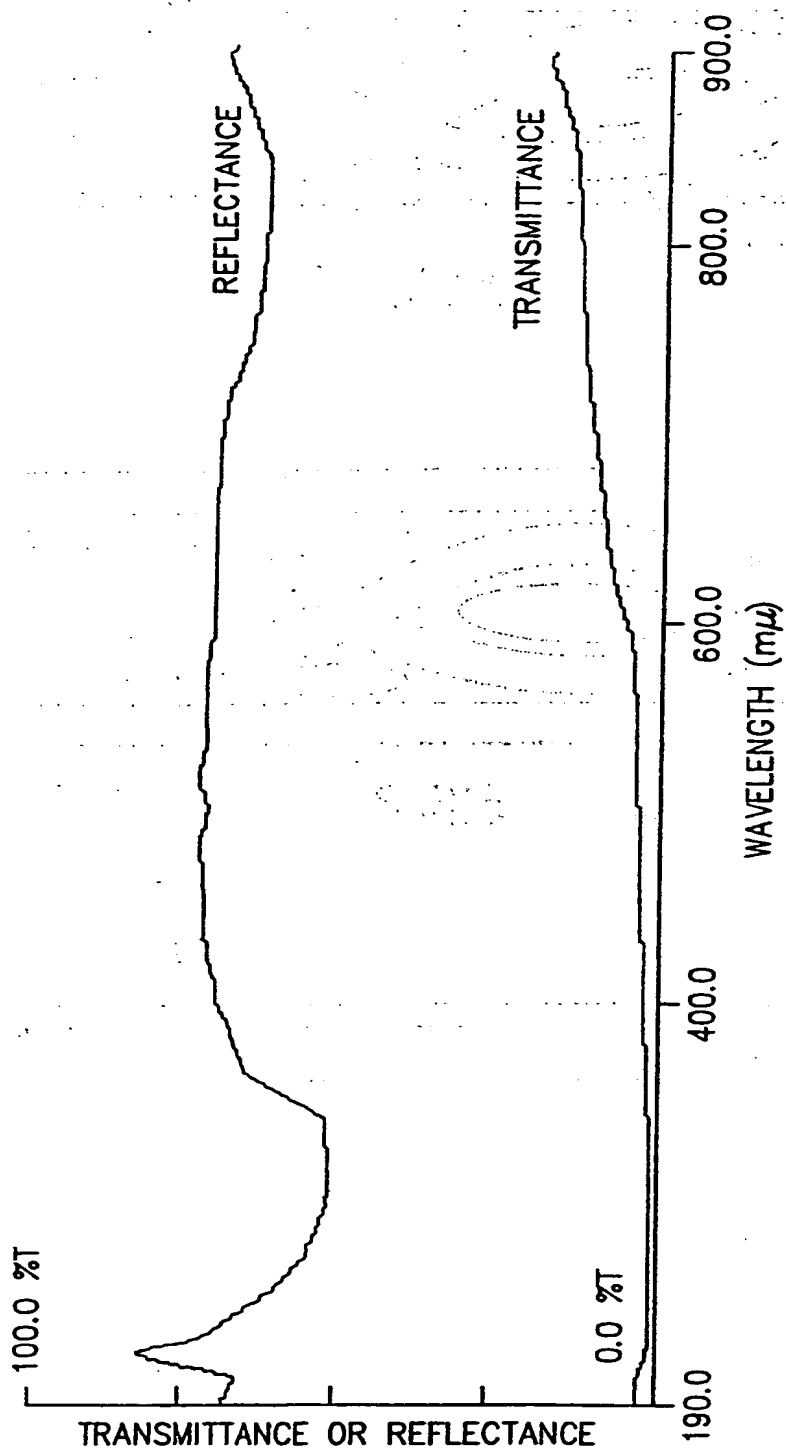
SUBSTITUTE SHEET

2/3

NATURAL SIDE FACING LIGHT SOURCE

TRANSMITTANCE 6.7 AVG.

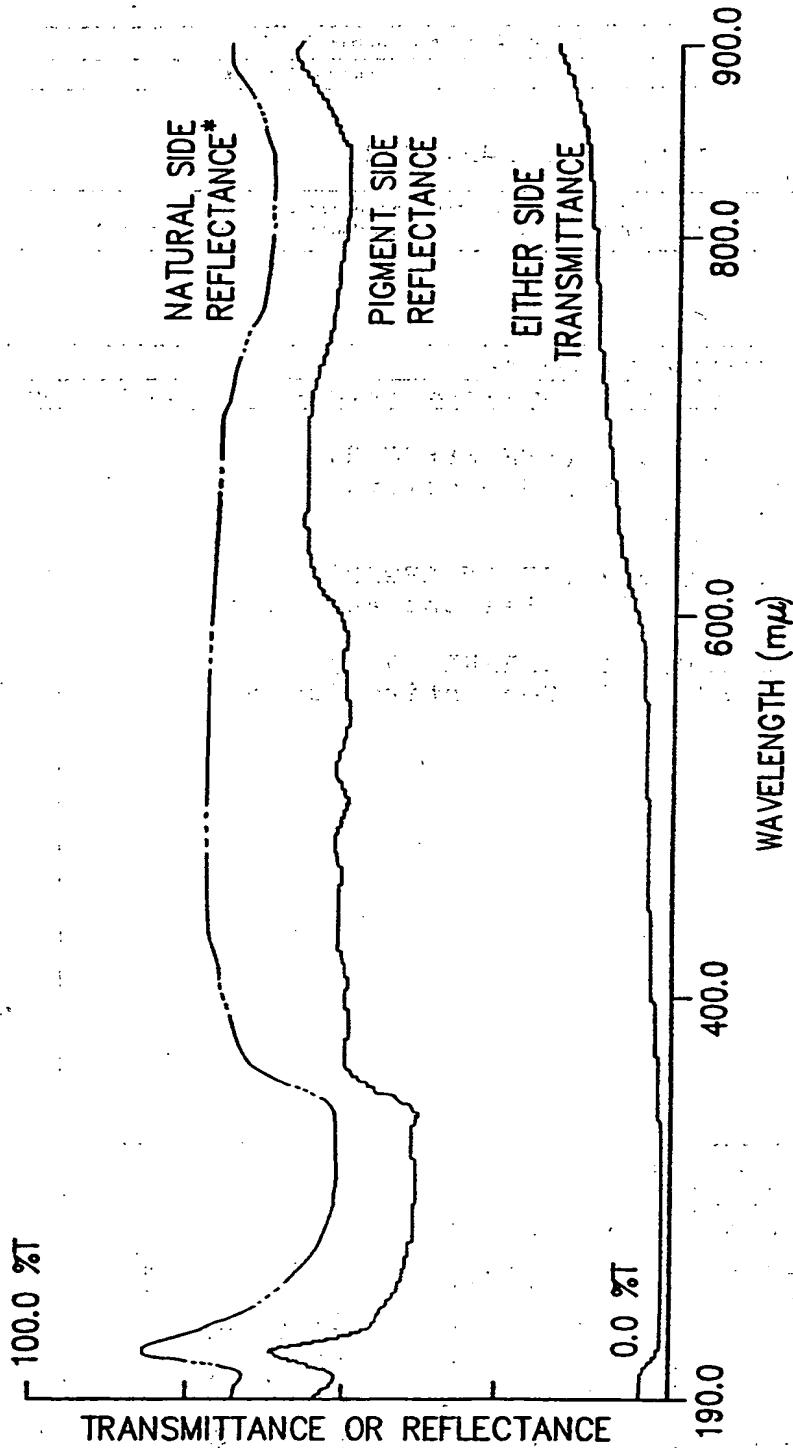
REFLECTANCE 68.5 AVG.



**FIG. 4**

**SUBSTITUTE SHEET**

BROWN SIDE FACING LIGHT SOURCE  
TRANSMITTANCE 7.2 AVG.  
REFLECTANCE 52.1 AVG.



**FIG. 5**

# INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US91/08675**

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) \*

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): B32B 27/00

U.S. CL. 428/421, 422, 245, 252

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System

Classification Symbols

U.S.

428/421, 422, 245, 252

Documentation Searched other than Minimum Documentation  
to the extent that such Documents are included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US, A, 4,610,918 (EFFENBERGER) 09 SEPTEMBER 1986; See column 2, lines 9-25 and Example 1.	1-3 & 10-12
X	US, A, 4,770,927 (EFFENBERGER) 13 SEPTEMBER 1988; See the Abstract.	1-3 & 10-12
Y	US, A, 3,850,674 (CLARKE, JR.) 26 NOVEMBER 1974; See entire document.	1-3 & 10-12

\* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not  
considered to be of particular relevance

"E" earlier document but published on or after the international  
filing date

"L" document which may throw doubts on priority claim(s) or  
which is cited to establish the publication date of another  
citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or  
other means

"P" document published prior to the international filing date but  
later than the priority date claimed

"T" later document published after the international filing date  
or priority date and not in conflict with the application but  
cited to understand the principle or theory underlying the  
invention

"X" document of particular relevance: the claimed invention  
cannot be considered novel or cannot be considered to  
involve an inventive step

"Y" document of particular relevance: the claimed invention  
cannot be considered to involve an inventive step when the  
document is combined with one or more other such docu-  
ments, such combination being obvious to a person skilled  
in the art.

"Δ" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

17 JANUARY 1992

Date of Mailing of this International Search Report

28 JAN 1992

International Searching Authority

ISA/US

Signature of Authorized Officer

E. Rollins Buffalow

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:
  
2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:
  
3. ☒ Claim numbers 4-9 & 13-21, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.